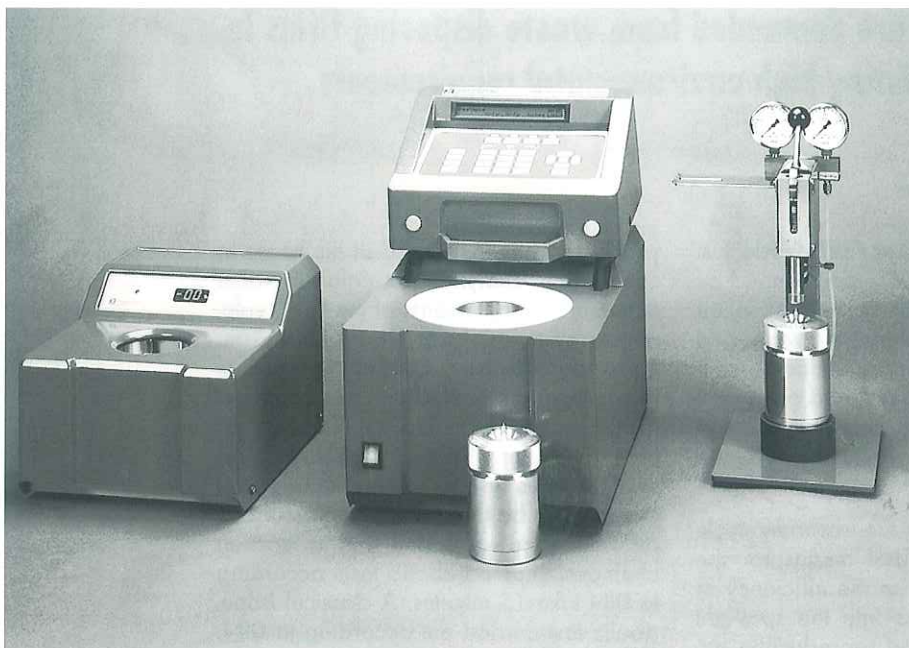


**Special printing from**  
**GIT 11/96**  
**LABORATORY-MAGAZINE**



## **Determination of Calorific-Values with Simultaneous Halogen and Sulfur Decomposition**

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# Determination of Calorific Values with Simultaneous Halogen and Sulfur Decomposition

In waste management, and especially in its analytic field, high standards are demanded from waste disposing firms in meeting the existing high environmental requirements.

It is not enough to dispose of waste just somehow. A qualified company knows by means of its declaration and identification analytics the composition of the waste and informs the waste producer about it, conducts advisory discussions and gives product-specific assistance. This way any possible environmental pollution will be effectively prevented.

On October 7, 1996 the economy cycle law became valid. That means for the waste management that the efficiency of their laboratories gets into the spotlight even more. Quick and reproducible analytics are here the basis for giving waste producers precise statements on use, recycling or disposal in waste disposal plants.

## DIN-Methods or HOUSE-Methods

Beside the DIN-methods, further recommendations as well as regulations are at hand for the determination of most different parameters. But not all of them are applied by the waste management in corresponding fields of investigation.

The house method resulted as a consequence of the above mentioned reasons, but also because of the demand for reproducible and informative analytic results to be faster and more efficient.

Rethmann Waste Management, Region West, Department Laboratory Marl, has paid attention to this problem for some

years, and has introduced in his house in combustion analytics the calorific value determination by means of the "dry" calorimeter system C7000 (Ill. 1) of Messrs. IKA-Analysentechnik. Contrary to classical decomposition methods, in this calorimetric process there is absolutely no water as heat transmitter. The main problem in classical aqueous systems is the relatively inert temperature balance with the pressurized decomposition vessel and with its reaction chamber. Thus adiabatic tests according to DIN take 15 minutes. A classical isoperibolic test carried out according to DIN, ISO or ASTM, takes about 20 minutes. With the help of the new calorimeter, it is now possible to obtain ISO 1928 measuring results in up to three minutes, whereby the temperature increase is measured as a result of the combustion directly in the decomposition vessel and not in the auxiliary medium water. Four high-resolution heat sensors as well as the thermodynamically updated calorimetric bomb effect a homogenous heat distribution and prevent occurring memory effects and/or carry-overs.

Comparative measurements of the combustion enthalpies were carried out with different waste, such as waste oils, solvents, dyes and lacquer sludge, resins, used filters and low-caloric solvent-water mixes etc. in the adiabatic as well as in the double-dry system. There were no unpermitted deviations compared to DIN-methods.

## AOD-Decomposition System

Today the user can choose from various decomposition methods in order to carry out a simultaneous halogen and sulfur decomposition. Established decomposition techniques are the methods according to Wickbold, Grote-Kreker and Schöninger.

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Another method is the bomb decomposition method. Especially this last method offers the most favourable characteristics of all systems mentioned because of its physical properties. Thus core temperatures of appr. 1200–1500 °C are obtained in a pure oxygen atmosphere in the course of a combustion, whereby for a short time pressures of several hundred bars are generated.

The ioschore, pressure-proof design of such vessels permits an active intervention into existing chemical balances. So are, for instance, the problems of sulfur decomposition neutralized insofar as during the combustion of substances containing sulfur acc. to the law of mass action and according to the regularities following Le Chatelier almost exclusively  $\text{SO}_3$  and thus precisely one sulfur species is formed (Ill. 2).

For a long time it was a disadvantage of the bomb decomposition method that the vessel was not anticorrosive. There were frequent carry-overs and matrix effects. Furthermore, an abrasion of the production material could not be avoided so that frequently increased heavy metal contaminations rendered a determination of the

KEYWORDS

Calorimetry, decomposition, AOD-System, calorific values, bomb decomposition

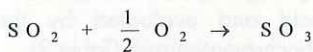


Ill. 1: The "doppeltrocken" calorimeter C 7000

contents by means of ionchromatography impossible.

With the development of the AOD-1 system, not only the last mentioned problems could be completely removed, but even more so, this system yields due to its completely new process course retrieval rates for all halogens, phos-

M W G :

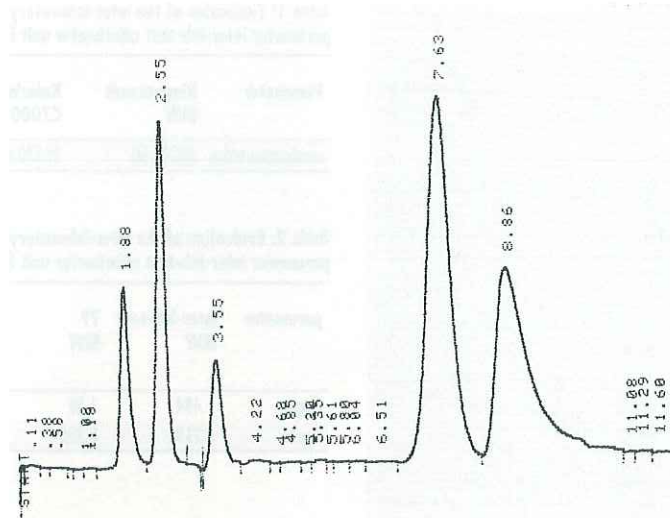


$$K_p = \frac{P_{\text{SO}_3}}{P_{\text{SO}_2} \cdot \sqrt{P_{\text{O}_2}}}$$

$$K_p \cdot \sqrt{P_{\text{O}_2}} = \frac{P_{\text{SO}_3}}{P_{\text{SO}_2}}$$

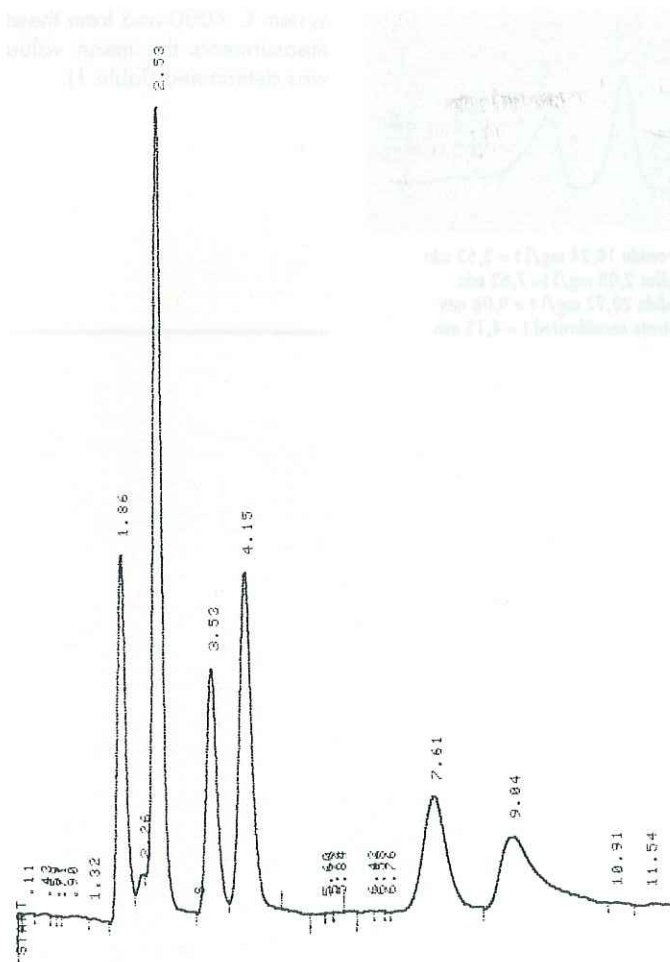
Ill. 2: Deviation of the MWG taking the  $\text{SO}_2$ -oxidation for an example.

phor, sulfur as well as various volatile metals that have not been obtained so far. Thus the already existing advantages of the bomb decomposition methods were further implemented and improved by important innovations. Basically unique were and are the extreme conditions in the decomposition system (p appr. 150–250 bar;  $T_{\text{core}}$  appr. 1200–1500 °C,  $T_{\text{gas}}$  appr. 500 °C). These properties have been supplemented by the selection of completely new, catalytically active materials. These are vessel inlets imbedded into the actual bomb body. These inlets consist of alloys that are catalytically activated by various conditioning steps. This especially is a catalyst which leads beside the reaction steps of Illustration 2 to a quantitative oxidation of the sulfur percentage into  $\text{SO}_3$ . A second catalyst was introduced into the system in



Ill. 3: Standard Chromatogram  
Fluoride 2,50 mg/l t = 1,88 min  
chloride 5,00 mg/l t = 2,55 min

bromide 5,00 mg/l t = 3,55 min  
sulfur 6,69 mg/l t = 7,63 min  
iodide 5,00 mg/l t = 8,86 min



Ill. 4: Chromatogram after decomposition in oxyhydrogen gas  
fluoride 5,91 mg/l t = 1,86 min  
chloride 14,85 mg/l t = 2,53 min

bromide 10,47 mg/l t = 3,53 min  
sulfur 2,12 mg/l t = 7,6 min  
iodide 21,84 mg/l t = 9,04 min  
nitrate uncalibrated t = 4,15 min

order to make even bromine and iodine measurable with retrieval rates of 97–100%.

Here especially the formation of elementary halogen species is prevented.

## Application Requirements in Bomb Decomposition

For an organic sample and/or an organically contaminated sample to be evaluated by means of potentiometric titration and/or ion-chromatography, it has to be submitted to a special preparation. The analytical principle is based upon a complete destruction of the organic sample matrix by way of combustion in the calorimetric bomb C7011 and/or in the decomposition system AOD 1 with an oxygen pressure of 30 bar.

- 1.) Weighed-in sample of appr. 0,5 g in an acetobutyrate capsule
- 2.) Admitting 8 ml absorption solution into the decomposition vessel. Absorption solution: 1,7 mmol sodium carbonate 1.8 mmol sodium hydrogen carbonate 12.5 ml/l of 30% hydrogen peroxide
- 2a.) Depending of the sample matrix, also 0,254 molar sodium hydroxide can be used.
- 3.) With low caloric samples a combustion aid should be used, in order to obtain a minimum temperature increase of 7 K (benzoic acid, polypropylen-balls or paraffin oil).

The samples were measured with an IC of Dionex SP 2000 i on the column LCK A 14 of Omnichrom at a column temperature of 70 °C.

Illustration 3 shows a standard chromatogram. Illustrations 4 and 5 show chromatograms of a solvent of the chemical industry containing halogen.

## Successful Participation in an Inter-Laboratory-Test

In October 1995, the Federal Association of German Waste Management placed a liquid waste sample at disposal for interested laboratories to check the quality of their investigation results. Beside the calorific value, total chlorine and total

**Table 1: Evaluation of the inter-laboratory-test for calorific value analytics  
parameter inter-lab-test calorimeter unit fluctuation range**

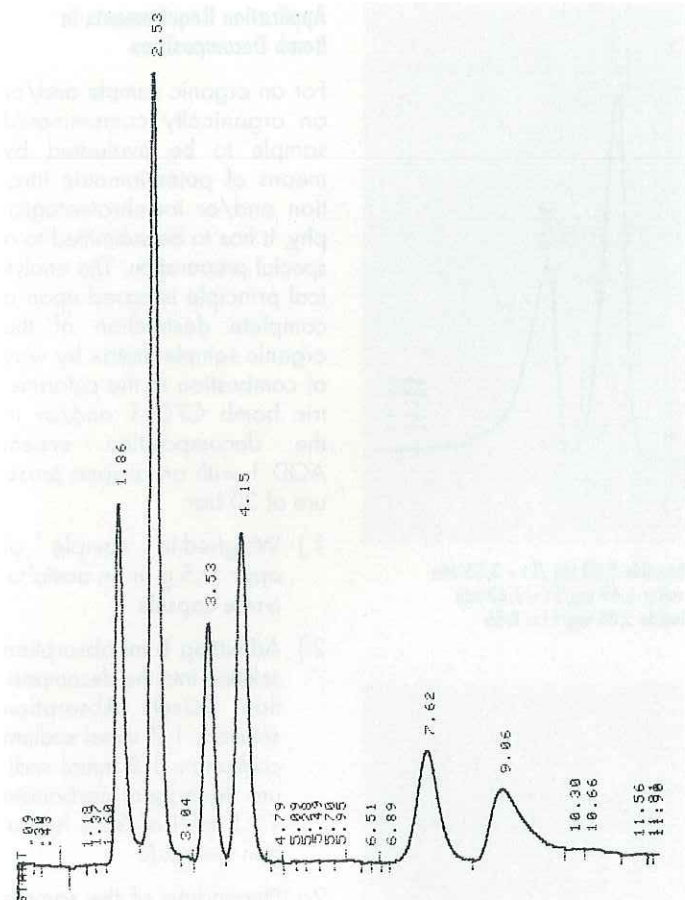
Parameter	Ringversuch MW	Kalorimeter C7000 MW	Einheit	fluctuation range inter-lab-test +/-
combustion value	26399.60	26520.00	J/g	540.28

**Table 2: Evaluation of the inter-laboratory-test for calorific value analytics  
parameter inter-lab-test calorimeter unit fluctuation range**

parameter	inter-lab-test MW	?? MW	?? ????MW	unit	fluctuation range inter- lab-test +/-
Cl ges.	1.494	1.59	1.575	Gew. %	0.273
S ges.	0.219	0.230	0.185	Gew. %	0.136

sulfur, another 10 parameters were to be investigated, which will here remain unmentioned. The calorific value was determined 4-fold in the double-dry system C 7000 and from these measurements the mean value was determined (Table 1).

The contents of total chlorine and total sulfur were mineralised by means of bomb decomposition as well as with the aid of oxygen and oxygen-hydrogen gas, decomposed 4-fold and evaluated by the ionchromatograph (Table 2).



**III. 5 Chromatogram after decomposition  
in the AOD-System**  
fluoride 6,17 mg/l t = 1,86 min  
chloride 14,60 mg/l t = 2,53 min

bromide 10,24 mg/l t = 3,53 min  
sulfur 2,08 mg/l t = 7,62 min  
iodide 20,92 mg/l t = 9,06 min  
nitrate uncalibrated t = 4,15 min